Final Report
ONR Project N000-14-91-J-1495

Project Title: *Chemical and physical processes which control the temporal and spatial variability of trace elements in the upper marine water column.*

Goals

The goal of the project was to identify the processes which control the temporal and spatial variability of two important trace elements, Cu and Mn, in the upper marine water column.

Objectives

The objective is to study the changes in speciation and total concentration of Cu and Mn at the Bermuda Atlantic Time Series (BATS) station over the period Jan 1992-Mar 1993 and interpret variability in terms of in situ chemical transformations (mediated by biological processes and light) and aeolian inputs of trace metals measured at nearby Bermuda by other workers. The station is characterized by strong seasonal forcing of physical, chemical and biological parameters. Also comparative studies of the behavior of Cu and Mn were made in two different oceanic environments: the permanently stratified Southern Sargasso Sea and the equatorial Pacific (Mn only). The objectives of these studies were to see if trends observed at BATS could be generalized to oceanic other environments and to see if empirical relationships established between physical and biological parameters and trace metal chemistry at BATS could be used to account for differences at these other environments.

Approach

The approach was a combination of laboratory and field measurements of Cu and Mn chemistry on several cruises to BATS at different seasons. Particle-solution reactions of Mn were studied at sea using radiotracers in freshly collected samples in order to estimate in situ rates of uptake. Samples were also collected for dissolved and particulate Mn analysis. The particle size spectra of particulate Mn was also measured, using an in situ pumping system. Results are being incorporated into a scavenging model of Mn using these data and incorporating the Price Weller Pinkel model of the diel mixed layer. For Cu, the distribution and organic complexation of this element has been studied at BATS using cathodic stripping voltammetry(CSV).

Tasks Completed

Five cruises to the Sargasso Sea were completed to the BATS station, during winter, spring summer fall and winter over the period from February 1992 to March 1993, under wide ranging conditions, with the mixed layer depth ranging from 20 to 200m. A permanently stratified station was studied in April 1992 in the southern Sargasso (26 N). Compilation and analysis of results from a cruise to the equatorial Pacific with Ken Bruland in 1991 was completed.

Results

At BATS, microbial Mn oxidation occurred throughout the year and was always the predominant pathway for Mn incorporation onto particles. Oxidation was significantly inhibited by light at levels as low as 4 % of surface PAR, and was almost completely inhibited at 40% PAR. Combining these data with underwater light measurements enabled us to predict in situ rates as a function of depth, but the actual rates determined on samples drawn for those depths were a more complex function of hydrography. When the mixed layer depth was shallow, Mn oxidation was inhibited throughout it. When the mixed layer depth was deep, Mn oxidation was observed even at the surface. Therefore, a more empirical approach is being used to incorporate the seasonal trends into the model. Attempts to measure photochemical action spectra from resuspended Mn oxides produced in natural samples were unsuccessful, due to low formation rates and breaking up of particles. As an alternative, samples were collected to isolate Mn oxidizing bacteria in culture, in collaboration with W. Ghiorse (Cornell), in order to have more material to work with, but we have not isolated a culture yet.

In equatorial Pacific, Mn uptake was dominated by non-oxidative, biological uptake. No Mn uptake was observed down to 200m. However, at that depth, uptake was dominated by oxidation. I speculate that these observations are probably due to the absence of Mn oxidizing bacteria in this environment. This could be due to the extremely low levels of Mn and other metals here, although enrichment studies with Mn and Fe did not lead to any increases in oxidizing activity. The contrasting behavior of Mn in the Sargasso Sea and equatorial Pacific indicates that more work is needed to establish what processes control Mn removal from the upper ocean globally.

The spatial variability of copper speciation was determined on each cruise. Speciation was dominated by a strong chelator which was present throughout the upper water column (resulting in very low free cupric ion levels) except under stratified conditions when it was absent from the mixed layer, which is probably due to photochemical degradation. The chelator may be produced by the marine cyanobacterium Synechococcus. Studies of Cu challenged Synechococcus cultures carried out with Larry Brand indicate that they produce a chelator with identical binding characteristics to the water column compound in response to Cu stress.

Accomplishments

The results show that Cu and Mn demonstrate considerable spatial and temporal variability in their chemical behavior in the upper water column, but much of the variability is consistent with what we have learned about their reactivity through shipboard incubation and speciation measurements. It provides a means for us to predict the response of these metals to changes in physical and biological parameters associated with seasonal or other changes.

Publications

Moffett, J.W. (1994). The contrasting behavior of Mn in the equatorial Pacific and Sargasso Sea (in prep).

Moffett, J.W. (1994). Competitive ligand exchange studies between Cu chelators in seawater using di beta-diketonates. (in prep).

Moffett, J.W. (1994). Spatial and temporal variability of copper complexation in the Sargasso Sea. (in prep).